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A Non-Traditional Vapor-Liquid-Solid Method for Bulk Synthesis of Semiconductor Nanowires

Shashank Sharma, and Mahendra K. Sunkara*
Department of Chemical Engineering, University of Louisville,
Louisville, KY 40292, USA
Guoda Lian and Elizabeth C. Dickey
Department of Chemical and Materials Engineering, University of Kentucky,
Lexington, KY 40506, USA
* Corresponding author: mahendra@louisville.edu

ABSTRACT

Multiple silicon nanowires were synthesized using large gallium pools and microwave plasma. Results showed that nanowires growing out of different sized large gallium drops show little variation in diameters, suggesting that our non-traditional technique can be used to synthesize bulk amounts of monodispersed nanowires out of thin films of molten gallium.

INTRODUCTION

Size constraints and surface effects induce novel characteristics in materials at nanoscale.[1-6] In order to utilize nanometer scale structures in applications such as electronic, optoelectronic, and catalytic, bulk amounts of nanostructures will be required with tunable composition and structure. In this regard, bulk synthesis of semiconductor nanowires has been traditionally achieved using several variations of transition metal catalyzed techniques such as vapor-liquid-solid (VLS). [7-20] In such techniques, the nanowire diameter is limited by the catalyst droplet size. However, creation of nanometer size catalyst droplets is a non-trivial task. Furthermore, given the fact that transition metals form high solubility eutectics with various semiconductor elements, it would be very difficult to obtain abrupt compositionally modulated structures. Nanowires have also been synthesized by restrictive growth methods such as nanotube-confined reactions [21-23] and with atomic scale step edges as templates. [24] In all of these techniques, it will be difficult to control the nanowire diameter and diameter distribution.

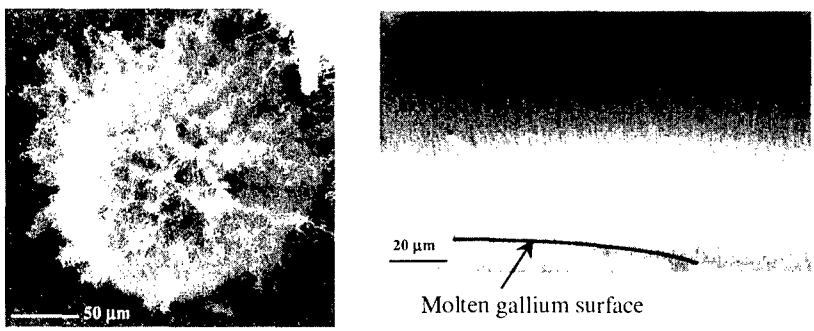
Recently our group demonstrated bulk synthesis of silicon nanowires using gallium as the molten metal solvent and microwave plasma to carry out the gas phase chemistry. [25] It was reported that multiple nuclei form and grow as nanowires out of a large gallium pool. Thus, this gallium and microwave plasma based technique eliminates the need for nanometer sized metal droplets and has a potential to work at much lower temperatures than the conventional techniques using transition metals. However, there are certain important aspects of this technique that remained unaddressed. In this paper, we discuss issues related to control over nanowire diameter and diameter distribution in our non-transition metal-based technique. We also present evidence for in-situ generation of silyl radicals thus confirming silicon source to be through gas phase.

EXPERIMENTAL DETAILS

The experimental setup for bulk synthesis of silicon nanowires has been previously described. [25] Chemical vapor transport experiments were also performed, in which gallium-covered p-BN and quartz substrates surrounded by silicon pieces were exposed to a diluted hydrogen plasma. An Ocean Optics® optical emission spectrometer (OES) was used to identify the various species in the plasma. Individual nanowires were analyzed for crystallinity and composition using high-resolution transmission electron microscopy (HRTEM) (200kV JEOL model 2010F) and energy-dispersive X-ray spectroscopy (EDX).

RESULTS AND DISCUSSIONS

Figure 1(a) shows a SEM micrograph of several fibers growing out of a large gallium pool after a typical growth experiment. Figure 1 (b) shows very straight silicon nanowires grown out of a gallium pool.



(a) (b)

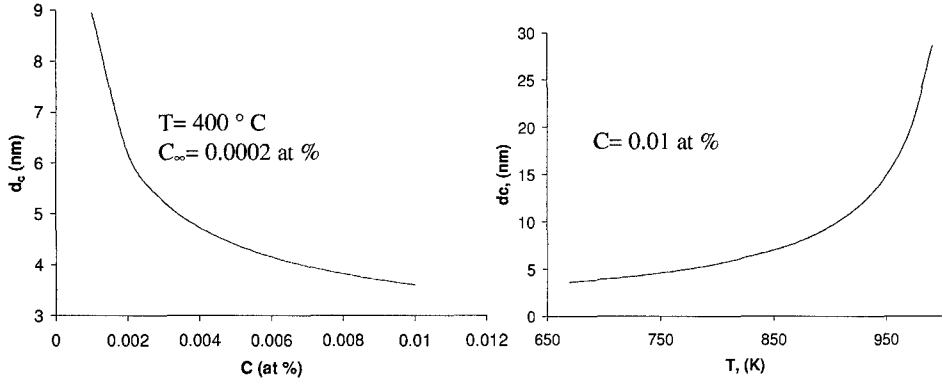
Figure1. (a) Multiple silicon fibers ~20 nm thick, grown out of a 200 µm gallium drop. (b) Straight silicon filaments ~25 nm thick, obtained after another experiments under different conditions.

In traditional VLS methods, nanowire diameter is determined by the transition metal droplet size. Thus, in order to obtain a uniform nanowire diameter distribution, monodispersed catalyst particles need to be created on a solid substrate. However, it has been reported that there is an inherent limitation in controlling the nanowire diameter. [27] Formation of the transition metal-Si alloy before nucleation causes the nanowires in general to be thicker than the metal droplet. Thus, it is difficult to absolutely control the nanowire diameter.

In our non-traditional technique discussed in this paper, the critical nuclei diameter can be defined based on the classical nucleation theory as

$$d_c = \frac{4\Omega\alpha}{RT \ln\left(\frac{C}{C_\infty}\right)} \qquad (1)$$

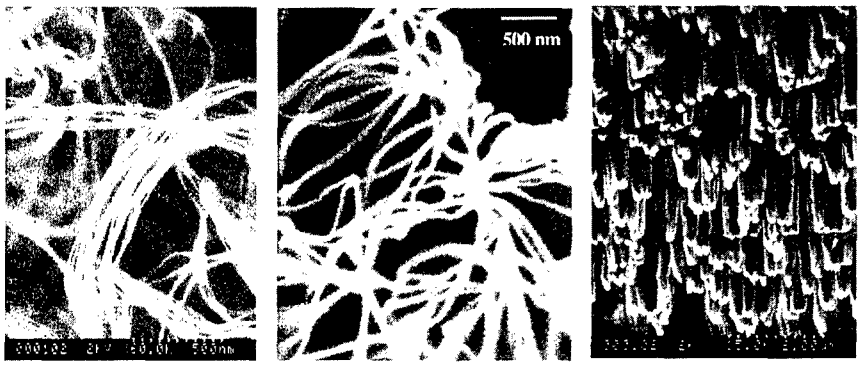
where, d_c, Ω, α, C and C_∞ represent critical nucleus diameter, molar volume, surface free energy, concentration of silicon within liquid alloy and equilibrium concentration at temperature T, respectively. Thus unlike in traditional VLS methods, the nanowire diameter in our technique is determined by the solute supersaturation in molten gallium and substrate temperature. Figure 2 shows variation of critical nucleus diameter as a function of temperature for a particular dissolved solute concentration and as a function of dissolved solute concentration at a particular temperature. It can be seen that at a specific dissolved silicon concentration in molten gallium, critical nucleus size increases with increasing temperature due to greater influence of temperature on the equilibrium solubility.



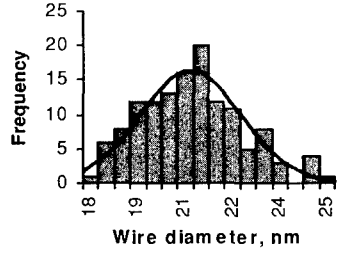
(a) (b)

Figure 2. Variation of the critical nucleus diameter defined by eqn (1) as a function of (a) dissolved solute concentration in molten gallium at a particular temperature, and (b) temperature for an arbitrary dissolved silicon concentration of 0.01 at %.

The liquid phase solute supersaturation is dependent on silicon supply at the V-L interface and the substrate temperature. The vapor phase silicon supersaturation is determined by substrate temperature, gas temperature, pressure, diluent gas and dilution fraction. Independent control over these parameters will enable a tighter control over nanowire diameter and diameter distribution. However in our current experimental setup, these parameters are related in a convoluted manner. Figures 2 (a)-(c) demonstrate that nanowires grown under different sets of experimental conditions have different diameters. Figure 2 (d) shows a representative diameter distribution of nanowires grown out of a 1.3 mm diameter gallium droplet at a substrate temperature of 700 ºC. For a particular set of experimental conditions, mean diameters of the nanowires grown out of different sized gallium droplets were very close to each other. Please see Table I. Thus it could be possible to synthesize silicon nanowires with a narrow diameter distribution using a thin film of gallium.



(a) (b) (c)



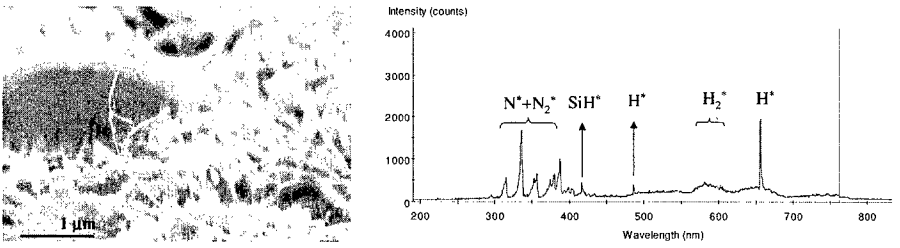
(d)

Figure 2. Bulk amounts of silicon nanowires obtained in three different experiments. Process parameters are (a) ~10 nm dia, 1000 W MW power, 30 torr total pressure, 0.25 sccm H_2/100 sccm N_2, 6 hrs (b) ~21 nm dia, 1000 W, 50 torr, 2.0 sccm H_2/100 sccm N_2, 4 hrs (c) ~150 nm dia, 900 W, 50 torr, 0.75 sccm H_2/100 sccm N_2, 5 hrs. (d) Diameter distribution of the nanowires grown under process conditions of (b); mean wire dia: 21.4 nm.

Table I. Mean nanowire diameters grown under different set of experimental conditions.

MW Power (W)	Pressure (Torr)	H2 flow rate in 100 sccm N2 (sccm)	Temperature (deg C)	Duration (hrs)	Droplet size (μm)	Mean wire dia (nm)	SD (nm)
850	40	0.8	580	12	800	24.2	0.8
850	40	0.8	580	12	1300	25.0	1.0
1000	50	2	695	4	71.75	35.3	2.8
1000	50	2	695	4	305	34.4	2.6
1000	50	2	695	4	1219	34.3	3.1
850	50	10	701	9	217.3	21.4	1.6
850	50	10	701	9	364.7	20.4	2.1

Gallium is not known to act as a catalyst for gas decomposition or dehydrogenation reactions. In our experiments, Silyl species are produced by atomic hydrogen etching of the exposed silicon substrate. In order to confirm this hypothesis, silicon nanowire growth experiments were performed using gallium covered non-silicon substrates surrounded by small silicon pieces. Figure 4 (a) shows silicon nanowires grown on a pyrolytic boron nitride substrate covered with Gallium droplets. Figure 4 (b) shows an optical emission spectrum taken during these chemical vapor transport experiments. A SiH peak was identified, [28-30] providing evidence of in-situ production of silyl radicals.



(a) (b)

Figure 3. (a) Silicon nanofibers obtained using PBN substrate covered with gallium droplets and surrounded by silicon pieces, exposed to the nitrogen plasma containing atomic hydrogen. (b) An optical emission spectrum of the plasma taken in the experimental conditions of (a).

CONCLUSIONS

It is possible to grow monodispersed silicon nanowires out of a gallium film using our non-traditional technique, as demonstrated by a very narrow diameter variation exhibited by the nanowires grown out of different sized gallium drops.

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